FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371	201/520 PCT US - Q106
	U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) 10/031022

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/USOO/19348	14 July 2000	16 July 1999

TITLE OF INVENTION

Lithium Thin Film Lamination Technology On Electrode To Increase Battery Capacity

APPLICANT(S) FOR DO/EO/US

Hisashi Tsukamoto

Chananit Sintuu

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☒ is attached hereto (required only if not communicated by the International Bureau).
   b. ☐ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☐ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☒ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☐ Other items or information:

531 Rec'd PCT/PTO 14 JAN 2002

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/051022	PCT/USOO/19348	201/520 PCT US - Q106

24. The following fees are submitted:.		CALCULATIONS PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :		
☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO	$1040.00	
☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	$890.00	
☐ International preliminary examination fee (37 CFR 1.445(a)(2)) paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	$740.00	
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)	$710.00	
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)	$100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =		$100.00
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).		$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	9 - 20 =	0	x $18.00	$0.00	
Independent claims	2 - 3 =	0	x $84.00	$0.00	
Multiple Dependent Claims **(check if applicable)**.			☐	$0.00	
TOTAL OF ABOVE CALCULATIONS =				$100.00	
Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				$0.00	
SUBTOTAL =				$100.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).			+	$0.00	
TOTAL NATIONAL FEE =				$100.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).**			☐	$0.00	
TOTAL FEES ENCLOSED =				$100.00	
				Amount to be: refunded	$
				charged	$

a. ☐ A check in the amount of _____ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. **500921** in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **500921** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Arthur Freilich
Freilich, Hornbaker & Rosen
P.O. Box 923127
Sylmar, CA 91392-3127

SIGNATURE

Arthur Freilich
NAME

19,281
REGISTRATION NUMBER

14 Jan 2002
DATE

Q106-PCT

LITHIUM THIN FILM LAMINATION TECHNOLOGY ON ELECTRODE TO INCREASE BATTERY CAPACITY

FIELD OF THE INVENTION

This invention relates to a method and apparatus for reducing the irreversible capacity of a rechargeable battery, in particular lithium ion batteries, in order to increase the battery's overall energy storage capacity.

BACKGROUND OF THE INVENTION

Batteries typically exhibit irreversible capacities after the initial cycle of charging. The significant capacity lost in the first cycle results in a loss in overall battery storage capacity. The irreversible capacity is due to the formation of the solid electrolyte interface (SEI) layer in typical negative electrodes from the first cycle of charging. However, other forms of irreversible capacity may be due to additional reasons, for example, cavities in the active material of the electrode structure may need to be initially filled with lithium ions before lithium ion insertion can proceed.

SUMMARY OF THE INVENTION

The present invention is directed to a method and apparatus for reducing the irreversible capacity of a lithium ion battery by initially depositing a layer of lithium metal onto or into the electrode structure. The deposited lithium serves to form the initial SEI layer before cycling to thus reduce the amount of irreversible capacity and increase the overall battery

storage capacity.

A typical electrode structure is comprised of a conducting metal substrate coated with an active material mixture. For example, a typical negative electrode consists of a copper substrate coated with a mixture of graphite and a binder such as polyvinyl di-fluoride (PVDF). In accordance with the present invention, a lithium layer is deposited onto or into the electrode active material to reduce the amount of irreversible capacity by filling voids in the active material that do not participate in the reversible lithium ion insertion process.

In accordance with a preferred embodiment, lithium metal is first deposited onto a carrier, which is then used to transfer the lithium metal to the electrode structure by the application of heat, vacuum, and/or pressure. The carrier preferably comprises a long strip of plastic substrate that is preferable for a continuous transfer of lithium onto or into the electrode. In addition, this approach lends itself to commercial production. The substrate could be one of several materials such as ortho-polypropylene (OPP), Polyethylene Terephthalate (PET), polyimide, or other type of plastic. Lithium metal can be deposited onto or into one or both surfaces of the substrate. The lithium-coated plastic and the electrode material are then placed between two rollers or two plates. Lithium is transferred onto or into the electrode active material by applying heat and/or pressure in vacuum. The rollers or plates are

heated in vacuum to about 120°C, or within the range of 25°C to 350°C. A pressure of 50 kg/cm^2 to 600 kg/cm^2 is applied to the rollers. Similarly, in the case of two plates, a pressure of 50 kg/cm^2 to 600 kg/cm^2 is applied to the sheets of material between them.

The speed of movement of the carrier electrode material through the roller pair or the plate pair is in the range of 10 cm/min. to 5 m/min. For a given speed, the length of time the materials are exposed to the heat and pressure rollers, or alternatively the heat and pressure plates, will be fixed, depending only on the lengthwise distance of the plate along the direction of the material movement. For the roller pair, deformation of the rollers results in distance in the direction of travel of the material, which adds to the actual contact time of pressure and temperature application. The method could be used for either single-sided coating or double-sided coating. In the double-sided coating method, both sides of the metal substrate are coated with active material. The coated metal substrate is then sandwiched between two lithium-coated plastic carriers, with the lithium sides facing the active material on the coated metal substrate. All three sheets are then fed into a mechanism for applying heat and/or pressure in vacuum. As a result, lithium is transferred to both sides of the electrode structure, i.e., the coated metal substrate.

The thickness of lithium transferred onto the electrode structure can be controlled to produce a lithium coating between about 50 Angstroms and

0.3 millimeters. Using this technology, it is expected to increase a lithium ion battery capacity by about 7% to 15%.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other features and advantages of the invention will be more apparent from the following detailed description wherein:

Figure 1 shows the electrode structure coated with active material;

Figure 2 shows the structure of the film of lithium metal deposited on the plastic substrate;

Figure 3A shows the roller pair system that will be used to transfer the lithium from the carrier to the electrode by applying heat and pressure in vacuum;

Figure 3B shows the plate pair system that will be used to transfer the lithium from the carrier to the electrode by applying heat and/or pressure in a vacuum atmosphere;

Figure 4 shows the first cycle of an example negative electrode, a SiO nano-composite electrode that has not been laminated with lithium.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following text describes the preferred mode presently contemplated for carrying out the invention and is not intended to describe all possible modifications and variations consistent with the spirit and purpose of the invention. This description is not to be taken in

a limiting sense, but is merely made for the purpose of describing the general principles and preferred manner of practicing the invention. The scope of the invention should be determined with reference to the claims.

The objective of this invention is to significantly reduce the irreversible capacity produced mainly from the first cycle life of the active material of an electrode. A reduction in the irreversible capacity will ultimately lead to an overall increase in battery capacity. Lithium is transferred to the electrode by lamination of lithium metal onto or into an electrode structure. This electrode structure has a metal conducting layer coated with an active material. For example, negative active material is typically a mixture of graphite and PVDF. The lamination of lithium metal onto or into the electrode structure will reduce the amount of irreversible capacity by readily supplying sufficient lithium to fill any voids in the active material, which do not participate in the reversible lithium insertion process.

Figure 1 shows the structure of an electrode (100), having a lithium coating (101) in accordance with the present invention. The substrate (103) for negative electrodes is usually copper foil but other types of material such as a copper-plated polymer may be used. However, it must be noted that the substrate should not react with lithium metal, which is why copper is most often used as the negative electrode

substrate. The metal of the electrode may be coated with, for example, a mixture of graphite and silicon oxide (102). A suitable mixture of about 20% SiO nano-composite and 80% graphite for a negative electrode has an ability to create a capacity of about 500 mAh/g as compared to graphite's theoretical capacity of 372 mAh/g. This results in a significant increase in the rechargeable capacity. However, such a mixture also has significant irreversible capacity, making the present invention greatly beneficial for such an electrode.

In order to laminate lithium metal (Figure 2, 201) to the electrode (100), the lithium (201) is deposited onto a carrier (202), which is then used to apply the lithium metal to the electrode structure. The carrier preferably comprises a long strip of plastic substrate.

Figure 3A details the process in which lithium will be transferred from the carrier substrate to the electrode. The left side of the figure is prior to lithium printing, while the right side is after lithium printing. The preferred embodiment consists of two rollers (305) or plates (Figure 3B, 306) with lithium plus carrier substrate (301) placed between the two rollers or plates. In addition, pressure will be applied to the rollers (Figure 3A, 305), or plates (Figure 3B, 306) and as the electrode (303) and lithium-deposited carrier substrate (301) move through the rollers (304), or plates, the lithium metal (201) will be laminated onto or into the electrode (100).

Figure 4 is a graph of the first cycle of a SiO nano-composite cell that has not been initially laminated with lithium metal. If the discharge curve is transposed along an imaginary axis, it is clear that there is a large initial irreversible capacity that must be reduced in order to increase battery capacity.

While the invention herein disclosed has been described by means of specific embodiments and applications thereof, numerous modifications and various could be made thereto by those skilled in the art without departing from the scope of the invention set forth in the claims.

CLAIMS

What is claimed is:

1. A method to laminate lithium onto an electrode comprising the steps of:
   (a) utilizing an electrode structure coated with active material consisting of, as a negative electrode example, a mixture of graphite and a binder;
   (b) utilizing lithium coated plastic sheet where in said plastic sheet is selected from the group consisting of oriented polypropylene (OPP) polyethylene Terephthalate, and polyimide;
   (c) pressing the said electrode material and said lithium coated material together using a pair of pressing structures;
   (d) applying pressure and heat in vacuum to said materials while they are pressed together by said pressing structures;
   (e) moving said materials though the pressing structures while applying continuous pressure and heat to said materials as they move through said pressing structures.
2. The method of claim 1 further comprising the step of utilizing the said laminated electrode in lithium or lithium ion batteries.
3. The method of claim 1 further comprising the step of utilizing a pair of rollers as the pressing structures.
4. The method of claim 1 further comprising the step of utilizing a pair of plates as the pressing structures.

5. The method of claim 1 further comprising the step of applying heat in a vacuum atmosphere by utilizing said pressing structures at a temperature within the range 25°C to 250°C.

6. The method of claim 1 further comprising the step of applying pressure in the range of 50 kg/cm^2 to 600 kg/cm^2 utilizing said pressure structures.

7. A method for increasing the storage capacity of a lithium ion battery including the steps of:

   (a) providing an electrode structure comprised of a metal substrate coated with active material; and

   (b) depositing lithium onto or into said active material to reduce cavities therein.

8. The method of claim 7 wherein said depositing step includes:

   (a) providing a sheet carrier bearing a layer of lithium metal; and

   (b) pressing said layer of lithium metal against said active material to transfer lithium onto or into said active material.

9. The method of claim 8 wherein said depositing step further includes:

   (a) applying heat and/or pressure in vacuum to said carrier and/or said electrode structure to facilitate transfer of said lithium.

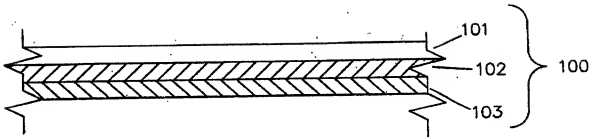

Fig 1

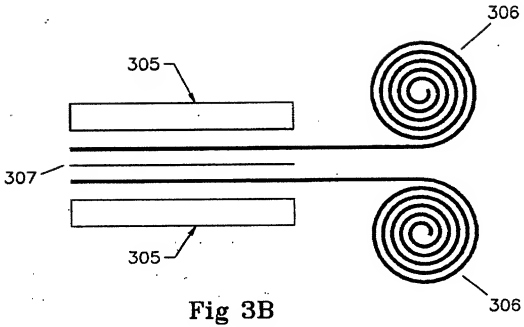

Fig 3B

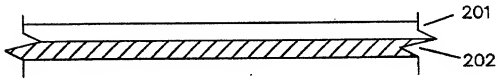

Fig 2

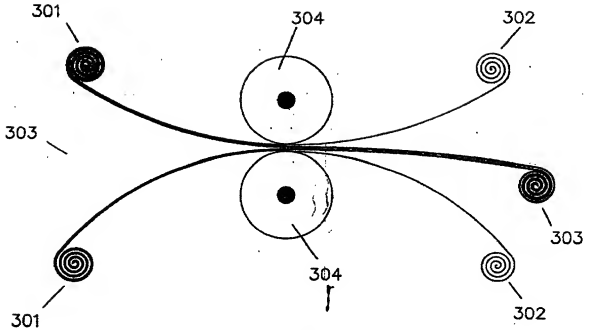

Fig 3A

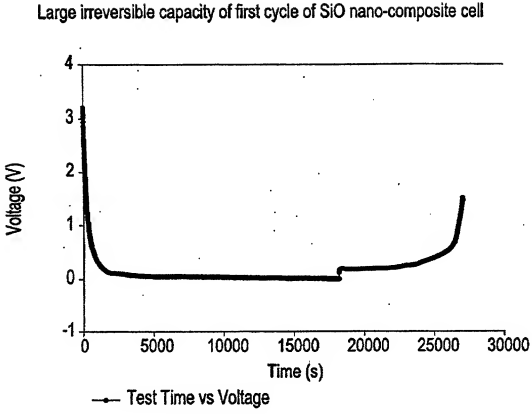

Fig 4

Any Docket 201/320 PCT US - Q108

DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled LITHIUM FILM LAMINATION TECHNOLOGY ON ELECTRODE TO INCREASE BATTERY CAPACITY the specification of which:

X is attached hereto.
— was filed on _____ as Application Serial No. _____
— and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56(a).

I hereby claim the benefit under 35 USC Section 120 of any United States application(s), or Section 365(c) of any PCT international application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of 35 USC Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, CFR, Section 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(1) International Application PCT/US00/19348 Filed 14 July 2000

I hereby appoint the following attorney(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

Arthur Freilich Reg. No. 19,281 Leon D. Rosen Reg. No. 21,077
Robert D. Hornbaker Reg. No. 19,965 Timothy T. Tyson Reg. No. 28,915

Address all telephone calls to: Arthur Freilich at 818-676-6406.
Address all correspondence to: Arthur Freilich
FREILICH, HORNBAKER & ROSEN
P.O. Box 923127
Sylmar, CA 91392-3127

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor HISASHI TSUKAMOTO

Inventor's Signature _____ Date _____

Residence 28445 Via Joyce Drive, Saugus, CA 91350

Citizenship U.S.

Post Office Address same as above

2-00

Full name second inventor CHANANIT SUNTIVI

Inventor's Signature Chananit Suntivi Date 1/14/02

Residence 15319 Brook Arbor Court, Houston, TX 77062 TX

Citizenship U.S.

Post Office Address same as above

QUA66.DEC 520 PCT.wpd

Atty Docket 201/520 PCT US - Q106

DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled LITHIUM FILM LAMINATION TECHNOLOGY ON ELECTRODE TO INCREASE BATTERY CAPACITY the specification of which:

X is attached hereto.
___ was filed on _____ as Application Serial No. _____
___ and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56(a),

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Address all telephone calls to: Arthur Freilich at 818-678-6408.
Address all correspondence to: Arthur Freilich
FREILICH, HORNBAKER & ROSEN
P.O. Box 923127
Sylmar, CA 91392-3127

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00

Full name of sole or first inventor HISASHI TSUKAMOTO

Inventor's Signature _____ Date 1-10-02

Residence 28445 Via Joyce Drive, Saugus, CA 91350 CA.

Citizenship U.S.

Post Office Address same as above

Full name second inventor CHANANIT SINTUU

Inventor's Signature _____ Date _____

Residence 15319 Brook Arbor Court, Houston, TX 77062

Citizenship U.S.

Post Office Address same as above